

All Nitrogen or High Nitrogen Compounds as High Energy Density Materials

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Executive Summary

The goals of this research were the identification of potential polynitrogen HEDM candidates and the design of strategies and experimental approaches for their attempted syntheses. This program was a Phase I Small Business Technology Transfer Program (STTR) contract with the Air Force Office of Scientific Research (Contract FA9550-04-C-0112). It was carried by ERC-Incorporated as the Small Business and the University of Southern California as the Academic Institution. The following goals have been accomplished:

1. The N_3^+ cation was identified as a promising HEDM target, and the feasibility of different synthetic approaches was evaluated.
2. It was shown that the previously reported claim for a bulk synthesis of N_5^- is invalid, and theoretical calculations were carried out to define favorable approaches for its synthesis.
3. The usefulness of a novel nitrogen-NMR technique for recording ^{15}N -spectra in natural abundance was demonstrated for N_5^+ and will be very useful for the identification of new polynitrogens.
4. The novel cation, N_2CN^+ , has been tentatively identified.
5. Numerous new polyazides have been prepared and characterized and demonstrate the potential of this family of compounds.
6. The novel N_3NOF^+ cation has been prepared and characterized. Tentative evidence has been obtained for the existence of a new exciting, room-temperature-stable $(\text{N}_3)_2\text{NO}^+$ cation.
7. The feasibility of using HOF for the oxygenation of nitrogen atoms was confirmed and has potential applications to polynitrogen chemistry.

Introduction

All-nitrogen and high-nitrogen compounds are highly energetic materials that hold great promise as rocket propellants or explosives. Theoretical performance calculations, carried out in our laboratory for the hypothetical cubic N_8 molecule and the ionic $N_5^+N_3^-$ salt, predicted specific impulse (I_{sp}) values of 503 and 421 sec, respectively. These are significant improvements over the benchmark monopropellant, hydrazine, with a theoretical I_{sp} value of 236 sec. An additional advantage of a polynitrogen propellant would be its low plume signature, which would greatly enhance its effectiveness for applications in tactical missiles.

The energy content of polynitrogen compounds arises from the energy difference between the average bond energies of nitrogen-nitrogen single, double and triple bonds. Contrary to most elements in the periodic system, the average bond energy of an N-N single bond (38 kcal/mol) is considerably less than $\frac{1}{2}$ of that of a double bond (100 kcal/mol) or $\frac{1}{3}$ of that of a triple bond (226 kcal/mol). Similarly, the average bond energy of an N=N double bond is considerably less than $\frac{2}{3}$ of that of a typical triple bond. Therefore, the decomposition of a polynitrogen compound, composed of nitrogen-nitrogen single and double bonds, to triply bonded dinitrogen is accompanied by a relatively large energy release. Because all the energy content of these materials stems from endothermicity and, normally, the sensitivity of energetic materials increases with increasing endothermicity, most of the known high-nitrogen compounds are extremely shock sensitive. Furthermore, all these compounds are thermodynamically unstable, and only a small number of them possess large enough barriers toward decomposition to provide them with sufficient kinetic stability to allow their safe handling. In view of these difficulties, it is not surprising that, up to date, only two polynitrogen species have been prepared in bulk as stable materials. These two compounds are the azide anion, N_3^- , (ref. 1) and the N_5^+

cation (ref. 2). The results from a recent combined experimental and theoretical study have shown (ref. 3) that the combination of these two ions does not result in the formation of a stable salt and that other ions or covalent polynitrogens are needed to provide potentially useful materials.

High-nitrogen compounds constitute a second area of significant interest. It is well known that the insertion of one hetero atom, such as carbon or oxygen, can greatly enhance the stability of a nitrogen compound. Therefore, these compounds might have better stability, while retaining much of the endothermicity. Furthermore, numerous polyazido compounds are known which combine high nitrogen content with reasonable stability (refs. 4). These compounds hold promise as initiators, gas generators, burning rate accelerators, and ingredients in solid or smokeless propellants.

Objectives

The overall objectives of this research were the syntheses and characterization of polynitrogen and high-nitrogen energetic materials that are useful as propellants or explosives ingredients. This program was part of a Small Business Technology Transfer Program (STTR) contract with the Air Force Office of Scientific Research (Contract FA9550-04-C-0112) and was carried out in close collaboration with the AFOSR Program, F49620-02-1-0229, at the University of Southern California.

Results

N_3^+ Cation: The N_3^+ cation is a promising candidate for replacing the N_5^+ cation. We have shown by theoretical calculations, carried out by Dave Dixon at the University of Alabama, that its activation energy barrier toward decomposition to ground state N^+ and N_2 exceeds 80 kcal/mol, and that the ion is vibrationally stable. In contrast to N_5^+ , it is derived from a

vibrationally stable radical. We have estimated the stabilities of N_3^+N_3^- and N_3^+N_5^- and found that these salts would be more stable than N_5^+N_3^- and N_5^+N_5^- .

We have explored several pathways towards the formation of N_3^+ . The first approach involved the reaction of FN_3 with very strong Lewis acids, such as SbF_5 . To test this approach, we first had to find a feasible and safe synthesis for the highly shock-sensitive FN_3 molecule. This hurdle was overcome by our discovery that HN_3 can be converted into FN_3 in quantitative yield by low-temperature fluorination with elemental fluorine in suitable solvents, such as freons. It was also shown that FN_3 forms an adduct with SbF_5 . Unfortunately, however, the α -nitrogen atom of FN_3 is a better donor than the fluorine atom, thus preempting fluoride abstraction and N_3^+ formation.

Our second approach toward N_3^+ involves the elimination of one molecule of N_2 from N_5^+ by either pyrolysis or photolysis. We have studied numerous samples of $\text{N}_5^+\text{SbF}_6^-$ which had been kept at or above room temperature for long time periods and had undergone partial decomposition. However, no evidence for N_3^+ could be detected by Raman and infrared spectroscopy. Therefore, it appears that controlled stepwise thermal N_2 elimination from solid N_5^+ salts is not feasible and low-temperature UV-photolysis, using solutions of $\text{N}_5^+\text{SbF}_6^-$ in solvents such as anhydrous HF, needs to be employed for supplying the required activation energy. We have calculated the energy difference between $\text{N}_5^+(^1\text{A}_1)$ and $\text{N}_3^+(\text{X}^3\Sigma_g^-) + \text{N}_2(^1\Sigma_g^+)$ to be only 10.2 kcal/mol or 28030 Å. Because elimination of a second N_2 molecule requires an additional 80.1 kcal/mol, it should be possible to limit the N_2 elimination to one molecule. To study this approach experimentally, we have prepared a sample of $\text{N}_5^+\text{SbF}_6^-$ and will record its IR/visible/uv spectra in HF solution which will allow us to select suitable irradiation sources.

Our third approach toward N_3^+ involves the reaction of $\text{XeF}^+\text{SbF}_6^-$ with $(\text{CH}_3)_3\text{SiN}_3$ at low temperature and is aimed at the unknown $\text{XeN}_3^+\text{SbF}_6^-$ salt. We have shown by theoretical calculations that the XeN_3^+ cation is vibrationally stable and that its decomposition to Xe and N_3^+ is energetically favored by 23.7 kcal/mol over that to Xe^+ and N_3 . Since the Xe-N bond is by far the weakest bond in this cation, gentle warming of $\text{XeN}_3^+\text{SbF}_6^-$ should result in Xe evolution and formation of $\text{N}_3^+\text{SbF}_6^-$. If the Xe-N bond strength requires a cleavage temperature which exceeds the thermal stability of N_3^+ , XeN_3^+ could be replaced by KrN_3^+ . The Kr-N bond is much weaker than the Xe-N bond, and formation of N_3^+ and Kr is favored by an even larger amount of energy, 66.3 kcal/mol, over that of Kr^+ and N_3 . However, the increased oxidizing power of KrF^+ could present a major compatibility problem between KrF^+ and $(\text{CH}_3)_3\text{SiN}_3$. We have prepared the required $\text{XeF}^+\text{SbF}_6^-$ starting material and have carried out preliminary screening reactions with $(\text{CH}_3)_3\text{SiN}_3$ to find a compatible solvent system. It was found that $\text{XeF}^+\text{SbF}_6^-$ attacks neat CH_3CN under formation of black decomposition products. Since the existence of stable $\text{CH}_3\text{CN}\cdot\text{XeF}^+$ adducts is known, we may have to pre-form these adducts in HF solution, remove the HF solvent and then add the excess of CH_3CN . Since the oxidizing power of the $\text{CH}_3\text{CN}\cdot\text{XeF}^+$ cation is considerably lower than that of XeF^+ , it is expected to be compatible with CH_3CN . The potential of SO_2 as a solvent system was also briefly explored, but again reaction of XeF^+ with the solvent was observed and more work will be required on this system.

N_5^- Anion: Significant progress was also made in the area of N_5^- chemistry. This anion was first observed by us using electrospray negative ion mass spectroscopy (ref. 5). In a subsequent paper (ref. 6), Butler from Ireland reported, based on NMR observations, a bulk synthesis for this ion. We have repeated his work, using isotopic substitution experiments, and have shown conclusively that his work is incorrect and that the resonance attributed by him to

N_5^- is actually due to the NO_3^- anion. The results were summarized in manuscript form and published in J. C. S. Chem. Commun. (ref. 7). In view of these results, a bulk synthesis of N_5^- still needs to be accomplished. We have carried out theoretical calculations which show that N_5^- favors the formation of σ -complexes over that of π -complexes, resulting in a loss of aromaticity for N_5^- and facilitating N_2 elimination. To circumvent this problem, we plan to complex the cations with crown-ethers. The resulting flat bulky cations are expected to favor sandwich structures and π -bonding.

Nitrogen-NMR Spectroscopy: Another area of great interest in polynitrogen chemistry dealt with the development of improved methods for the identification of novel compounds. A powerful method for the characterization of polynitrogen compounds is nitrogen-NMR spectroscopy. This method, however, suffers from a major drawback. The ^{14}N isotope, which has a natural abundance of 99.4 %, has a large quadrupole moment resulting in most cases in so much line-broadening that resonances are difficult or impossible to observe. By contrast, the ^{15}N isotope has no quadrupole moment and gives rise to sharp signals, however, its natural abundance of 0.36%, combined with long relaxation times on the order of one minute, makes the observation of ^{15}N -NMR spectra in natural abundance extremely difficult, requiring very expensive and time-consuming enrichment experiments. This problem was overcome in collaboration with Prof. Howard Taylor of USC. He has developed a new signal processing technique which allows the measurement of ^{15}N spectra in natural abundance and the observation of nitrogen-nitrogen spin-spin coupling with reasonably short measuring times. This method was successfully demonstrated by us for a sample of N_5^+ . Its complete NMR spectrum was observed and analyzed for the first time, and the results are being written up for publication. This method

will be extremely useful for the characterization and identification of new polynitrogen compounds.

N_2CN^+ Cation: We have studied the reaction of N_2F^+ with HCN in an effort to prepare the novel N_2CN^+ cation. Preliminary results indicate that we may have indeed prepared N_2CN^+ . ^{13}C substitution experiments resulted in isotopic shifts which are compatible with our theoretical predictions, but further work, including ^{15}N substitution, will be needed to verify our conclusions.

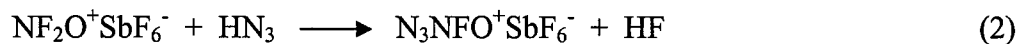
Polyazide Chemistry: In the area of polyazide chemistry, impressive progress was made and the following novel polyazides were prepared and characterized by vibrational spectroscopy and their crystal structures: $[Ta(N_3)_7]^{2-}$, $[Nb(N_3)_7]^{2-}$, $ONb(N_3)_3$, $[ONb(N_3)_5]^{2-}$, $[OMo(N_3)_5]^{2-}$, $[O_2Mo(N_3)_4]^{2-}$, $[O_2W(N_3)_4]^{2-}$, $O_2U(N_3)_2$, and $[O_2U(N_3)_4]^{2-}$. In addition, a uranium azide, probably $U(N_3)_6$, has been prepared, but so far was not completely characterized because of its sensitivity. The $[Ta(N_3)_7]^{2-}$ and $[Nb(N_3)_7]^{2-}$ anions exhibit, contrary to the related mono-capped octahedral heptafluoride anions WF_7^- and MoF_7^- (ref. 8), monocapped trigonal prismatic arrangements (2:4:1 structures). The $[O_2Mo(N_3)_4]^{2-}$ and $[O_2W(N_3)_4]^{2-}$ anions are isostructural, with the oxygens being *cis* with respect to each other. The $[OMo(N_3)_5]^{2-}$ anion has a pseudo-octahedral structure with the molybdenum in the oxidation state of (+V). It was obtained from the Mo(+VI) compound, $OMo(N_3)_4$, and azide ion in a redox reaction. The similar $[ONb(N_3)_5]^{2-}$ anion also shows a pseudo-octahedral arrangement of the ligands but, somewhat surprisingly, the orientation of the azide ligands is different. Its parent compound, $ONb(N_3)_3$ was also prepared and characterized by vibrational spectroscopy and theoretical calculations. The reaction of UF_6 with $(CH_3)_3SiN_3$ produced a highly sensitive black uranium azide, which probably is $U(N_3)_6$. From O_2UF_2 and TMS-azide the $O_2U(N_3)_2$ molecule was prepared which, in the presence of

azide ions, was converted to the $[trans-O_2U(N_3)_4]^{2-}$ anion, as shown by its crystal structure. All these compounds are highly energetic materials and powerful explosives. We have also prepared and structurally characterized all the members of the series of $[Ph_4E]N_3$ ($M = P, As, Sb$), which serve as excellent examples for the transition from ionic to covalent main group azides.

N_3NOF^+ and $(N_3)_2NO^+$ Cations: Our recent successful synthesis (ref. 2) of the N_5^+ cation (Eq. 1)

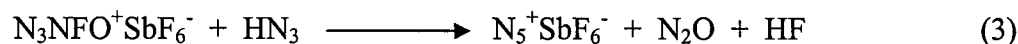


prompted us to explore the reactions of other nitrogen fluoride cations with HN_3 . A logical candidate for this type of chemistry was the NF_2O^+ cation (ref. 9). When $NF_2O^+SbF_6^-$ was reacted with either stoichiometric amounts or excess of HN_3 in anhydrous HF solution at temperatures ranging from -45 to -15 °C, one of the fluorine ligands was readily replaced by an azide group (Eq. 2).



The fluorine/azide exchange was limited to one fluorine ligand. Even when the reaction mixture was warmed towards room temperature, only decomposition of $N_3NFO^+SbF_6^-$ was observed, but no evidence for the formation of the $(N_3)_2NO^+$ cation was detected.

The $N_3NFO^+SbF_6^-$ salt is a white solid which is marginally stable at room temperature. It is highly soluble in anhydrous HF and, at room temperature, decomposes in an $H_2N_3^+HF_2^- \cdot nHF$ containing environment (HF solution) according to (Eq. 3).

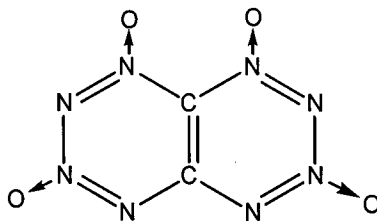


The formation of $N_5^+SbF_6^-$ might be explained by either the intermediate formation of $(N_3)_2NO^+SbF_6^-$, followed by N_2O loss, or, more likely, N_2O loss from $N_3NFO^+SbF_6^-$ to give $N_2F^+SbF_6^-$ which can react with HN_3 according to Eq. 1 to produce $N_5^+SbF_6^-$ (ref. 2). The $N_3NFO^+SbF_6^-$

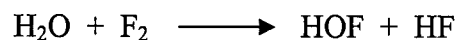
salt was identified by Raman, IR and ^{19}F , ^{14}N and ^{15}N NMR spectroscopy. The cation is planar and can exist in the form of two stereo isomers, depending on whether the azido group and the fluorine ligand are *cis* (z-isomer) or *trans* (e-isomer) with respect to each other. Surprisingly, the strength of the N-F bond in the two isomers is significantly different, with that in the z-isomer being weaker. This weakening is attributed to interaction between the F and N_γ atoms, as evidenced by the through-space-coupling, observed in the NMR spectra. The results are being written up for publication.

When carrying out reaction (2) not in HF but in a different solvent, such as SO_2 , in which the HN_3 is not protonated, replacement of the second fluorine atom in NF_2O^+ appears to be possible. Based on Raman spectroscopy, tentative evidence for the formation of a room temperature-stable $(\text{N}_3)_2\text{NO}^+$ cation has been obtained. This would constitute a major breakthrough and would be pursued in a Phase II follow-on, if granted, with high priority.

Stabilization of Polynitrogen Chains by Oxygen Substitution: A large body of work was carried out in Russia at the Zelinsky Institute by Tartakovskii's group, showing that the stability of catenated heterocyclic nitrogen atoms can be enhanced by introducing alternating charges (AC-compounds). The required alternation of the electronegativities of the nitrogen atoms was achieved by adding to every second nitrogen atom an oxygen atom. Although the stabilizing effect by alternate oxygen substitution was proven, the synthetic methods used were very cumbersome, and desired target compounds, such as DTTO,



have not been reported. Recent studies by Rozen (ref. 10) have shown that HOF, generated *in-situ* by passing elemental fluorine into wet CH₃CN,



is a powerful oxygenating agent which can be applied to the synthesis of N-oxides. In collaboration with Dr. Etzkorn and Profs. Prakash and Olah of USC, we have successfully confirmed the feasibility of Rozen's approach for adding two oxygen atoms to 1,10-phenantrolin.

Personnel Supported

Dr. Karl O. Christe

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Publications

- (1) "New High Energy Density Materials. Synthesis and Characterization of N₅⁺P(N₃)₆⁻, N₅⁺B(N₃)₄⁻, N₅⁺HF₂⁻·nHF, N₅⁺BF₄⁻, N₅⁺PF₆⁻, and N₅⁺SO₃F⁻," by R. Haiges, S. Schneider, T. Schroer, K. O. Christe, Angew. Chem. Int. Ed., **43**, 4919 (2004).
- (2) "The NH₃Cl⁺ Cation," by S. Schneider, R. Haiges, T. Schroer, J. Boatz, K. O. Christe, Angew. Chem. Int. Ed., **43**, 5213 (2004).
- (3) "Polyazide Chemistry. Preparation and Characterization of As(N₃)₅, Sb(N₃)₅, and [P(C₆H₅)₄][Sb(N₃)₆]," by R. Haiges, J. A. Boatz, A. Vij, V. Vij, M. Gerken, S. Schneider, M. Yousufuddin, K. O. Christe, Angew. Chem. Int. Ed., **43**, 6676 (2004).

- (4) "Polyazide Chemistry. Preparation and Characterization of the First Binary Group 6 Azides, $\text{Mo}(\text{N}_3)_6$, $\text{W}(\text{N}_3)_6$, $[\text{Mo}(\text{N}_3)_7]^-$ and $[\text{W}(\text{N}_3)_7]^-$ and of the $[\text{NW}(\text{N}_3)_4]^-$ and $[\text{NMo}(\text{N}_3)_4]^-$ Anions," by R. Haiges, J. A. Boatz, R. Bau, S. Schneider, T. Schroer, M. Yousufuddin, K. O. Christe, Angew. Chem. Int. Ed. 44, 1860 (2005) (VIP Paper).
- (5) "The race for the first generation of the pentazolate anion in solution is far from over," by T. Schroer, R. Haiges, S. Schneider, K. O. Christe, *J. Chem. Soc., Chem. Commun.* 1607 (2005).
- (6) "Experimental Evidence for Linear Metal-Azide Bonds. The Binary Group 5 Azides $\text{Nb}(\text{N}_3)_5$, $\text{Ta}(\text{N}_3)_5$, $[\text{Nb}(\text{N}_3)_6]^-$ and $[\text{Ta}(\text{N}_3)_6]^-$, and 1:1 Adducts of $\text{Nb}(\text{N}_3)_5$ and $\text{Ta}(\text{N}_3)_5$ with CH_3CN ," by Ralf Haiges, Jerry A. Boatz, Thorsten Schroer, Muhammed Yousufuddin, and Karl O. Christe, Angew. Chem. Int. Ed., in press.
- (7) "The Syntheses and Structures of $[\text{Ph}_4\text{E}]\text{N}_3$ ($\text{M} = \text{P}, \text{As}, \text{Sb}$), an excellent Example for the Transition from ionic to covalent Main Group Azides," by Ralf Haiges, Thorsten Schroer, Muhammed Yousufuddin, Karl O. Christe, *Z. Anorg. Allgem. Chem.*, in press.

Interactions/Transitions

Lectures were presented at the following conferences and universities:

A Frontier of Chemistry: New Species, Special Symposium, University of Helsinki, Finland, Dec. 2004.

17th Winter Fluorine Conference of the American Chemical Society, St. Pete, FL (2 papers), Jan. 2005.

229th National ACS Meeting, San Diego, CA, March 2005.

Molecular Dynamics Conference, Monterey, CA, May 2005.

Joint projects have been carried out with the following groups and colleagues:

Prof. Schrobilgen, McMaster University, Canada

Prof. Dixon, University of Alabama, Tuscaloosa

Dr. Feller, Pacific Northwest National Laboratory

Prof. Klapoetke, University of Munich, Germany

Prof. Jenkins, University of Warwick, UK

Profs. Prakash and Olah, and Dr. Etzkorn, University of Southern California

Prof. Bau and Muhammed Yousufuddin, University of Southern California

Prof. Telser, Roosevelt University, Chicago, IL

Profs. Taylor and Reisler, University of Southern California

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